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An unusual sandwich-type nickel oxide-siloxanolate complex $\{[\text{PhSiO}]_6(\mu_4\text{-O})_2(\mu_3\text{-O})_4[\text{Ni}_8(\mu_3\text{-O})_2](\mu_3\text{-O})_4(\mu_4\text{-O})_2[\text{PhSiO}]_6\} \cdot 14n\text{-BuOH} \cdot 10\text{H}_2\text{O} \cdot 2\text{Me}_2\text{CO}$. Synthesis and crystal structure

M.M. Levitsky, O.I. Schegolikhina, A.A. Zhdanov, V.A. Igonin, Yu.E. Ovchinnikov, V.E. Shklover and Yu.T. Struchkov *

A.N. Nesmeyanov Institute of Organo-Element Compounds, U.S.S.R. Academy of Sciences, Vavilov St. 28, 117334, Moscow (U.S.S.R.)

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Abstract

An X-ray crystal study of the nickel oxide-siloxanolate complex $\{[\text{PhSiO}]_6(\mu_4\text{-O})_2(\mu_3\text{-O})_4[\text{Ni}_8(\mu_3\text{-O})_2](\mu_3\text{-O})_4(\mu_4\text{-O})_2[\text{PhSiO}]_6\} \cdot 14n\text{-BuOH} \cdot 10\text{H}_2\text{O} \cdot 2\text{Me}_2\text{CO}$ (I or Ia without noncoordinating solvate molecules) having a cage structure has been carried out. The complex studied was prepared by the interaction of NiCl_2 with the product of the reaction of phenylsilsesquioxane $(\text{PhSiO}_{1.5})_n$ with NaOH . The polynuclear cage-like centrosymmetric molecule Ia has a sandwich-type structure. The inner two-dimensional nickel oxide fragment $\text{Ni}_8\text{O}_2(\mu\text{-O})_{12/2} = \text{Ni}_8\text{O}_8$ is structurally identical to a fragment of the NiO crystal layer which is one Ni atom thick and parallel to the (111) plane. All Ni atoms have oxygen atoms in an octahedral coordination (oxide, silanolate, molecules of water, butanol and acetone). The O atoms of the nickel oxide layer have both trigonal pyramidal ($\mu_3\text{-O}$) and distorted tetrahedral ($\mu_4\text{-O}$) coordination. The nickel oxide layer is bonded by Ni–O–Si bridges through silanolate O atoms with two outer 12-membered hexasiloxane $(\text{SiO})_6$ cycles (sandwich “caps”) with an almost ideal crown conformation. Some of the butanol and H_2O crystallosolvate molecules do not coordinate the Ni atoms being included in the cavities between Ia molecules. The NiO bond lengths are 2.006–2.159 Å, while the average Si–O(Si) and Si–O(Ni) bond lengths are 1.637 and 1.618 Å, respectively.

Introduction

At the present time hybrid (internally by heterodesmic) molecular systems, including siloxane fragments and fragments of transition metal oxide structures, viz. polymetallaorganosiloxanes (PMOS), are attracting great interest owing to their catalytic properties [1] and as models in studying both the structural and physicochemical properties of metal and semiconductor surfaces modified with siloxane coatings [2]; the latter use is important for the development of modern technologies devoted to the production of new solid materials. The peculiarities of PMOS, in particular the dependence of their complex framework oligomeric struc-

ture on synthesis conditions as well as the starting organosilicon compounds, have not been studied in any detail. At the same time, according to modern concepts [3] the PMOS structures (and consequently their physicochemical properties) are governed by synthesis conditions along with the coordination state of the metal atoms. Individual oligomeric PMOS, i.e. structural precursors of corresponding metallasiloxane polymers, should be isolated and their X-ray crystal structure determined in order to study systematically the structure and properties of polymeric PMOS and materials based on them.

The structure of the first individual PMOS (prepared from a trifunctional organosilicon compound), viz. the trimeric anionic cobaltaphenylsilsesquioxane $\text{Na}_6[(\text{PhSiO}_{1.5})_{22}\text{Co}_3\text{O}_6] \cdot 7\text{H}_2\text{O}$ (II) was studied previously [4].

The present paper continues the structural investigation of oligomeric PMOS prepared from polyfunctional organosilicon monomers. The main procedure for the preparation of oligomeric PMOS is based on the interaction between sodium silanolates and transition-metal halides (in the present case NiCl_2).

Discussion

General description of the structure

The studied crystal I is built from neutral centrosymmetric cage-like molecules $\{[(\text{PhSiO})_6]_2(\mu\text{-O})_{12}[\text{Ni}_8\text{O}_2]\}$ and a great number of solvate molecules ($14n\text{-BuOH}$, $10\text{H}_2\text{O}$, $2\text{Me}_2\text{CO}$), some of which participate in the coordination of Ni atoms (Fig. 1). The main bond lengths and bond angles are given in Tables 1 and 2.

The two-dimensional octanuclear nickel oxide framework $\text{Ni}_8\text{O}_2(\mu\text{-O})_{12/2} = \text{Ni}_8\text{O}_8$ is sandwiched between two cyclohexasiloxanolate hexadentate ligands

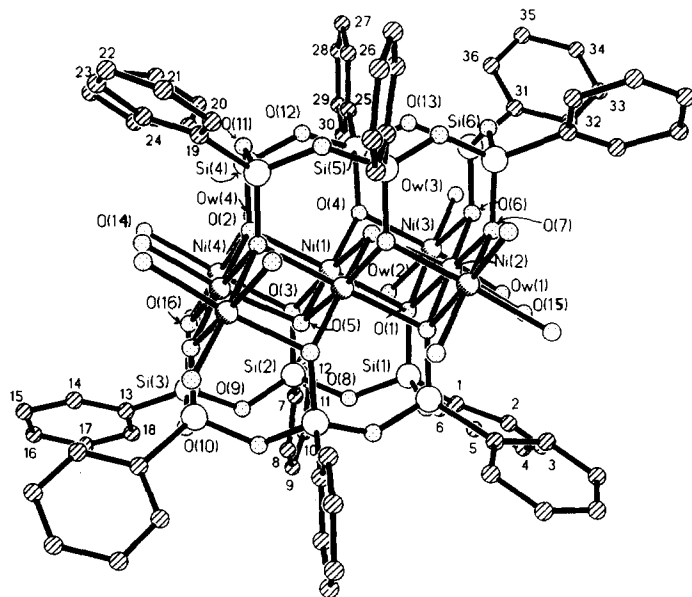


Fig. 1. General view of molecule Ia (only the O atoms are shown in coordinating butanol and acetone molecules).

Table 1

Main bond lengths (Å) in the nickel oxide–siloxane framework ^a

Ni(1)-O(1)	2.171(9)	Si(1)-O(1)	1.628(9)
Ni(1)-O(2)	2.176(9)	Si(1)-O(8)	1.634(9)
Ni(1)-O(3)	2.084(8)	Si(1)-O(11')	1.63(1)
Ni(1)-O(4)	2.092(8)	Si(1)-C(1)	1.89(1)
Ni(1)-O(5)	2.076(8)	Si(2)-O(3)	1.595(9)
Ni(1)-O(5')	2.069(8)	Si(2)-O(8)	1.65(1)
Ni(2)-O(1)	2.159(8)	Si(2)-O(9)	1.652(9)
Ni(2)-O(2')	2.125(8)	Si(2)-C(7)	1.89(1)
Ni(2)-O(5')	2.063(9)	Si(3)-O(7')	1.613(9)
Ni(2)-O(6)	2.065(9)	Si(3)-O(9)	1.644(9)
Ni(2)-O(7)	2.024(8)	Si(3)-O(10)	1.65(1)
Ni(2)-O(14)	2.130(9)	Si(3)-C(13)	1.85(2)
Ni(3)-O(1)	2.115(8)	Si(4)-O(2)	1.623(9)
Ni(3)-O(4)	2.057(9)	Si(4)-O(11)	1.633(9)
Ni(3)-O(6)	2.006(9)	Si(4)-O(12)	1.646(9)
Ni(3)-O _w (1)	2.15(1)	Si(4)-C(19)	1.89(2)
Ni(3)-O _w (2)	2.088(9)	Si(5)-O(4)	1.615(9)
Ni(3)-O _w (3)	2.11(11)	Si(5)-O(12)	1.609(9)
Ni(4)-O(2)	2.103(8)	Si(5)-O(13)	1.64(1)
Ni(4)-O(3)	2.069(9)	Si(5)-C(25)	1.86(2)
Ni(4)-O(7')	2.029(9)	Si(6)-O(6)	1.614(9)
Ni(4)-O(15)	2.12(1)	Si(6)-O(10')	1.617(9)
Ni(4)-O(16)	2.053(9)	Si(6)-O(13)	1.64(1)
Ni(4)-O _w (4)	2.091(9)	Si(6)-C(31)	1.87(1)

^a Two atoms with the same number but with and without a prime are related by an inversion centre.

(PhSi(μ -O)O)₆ linked with the Ni²⁺ atoms having octahedral coordination through the bridging O atoms of deprotonated silanolate groups. Thus, structure I differs fundamentally from that of the trimeric cobaltaphenylsilsesquioxane II [4], wherein the Co atoms replace some of the Si atoms in the silsesquioxane frame, have tetrahedral coordination and are not linked by the O bridges.

In addition to 12 μ_3 - and μ_4 -bridging silanolate O atoms and two oxide μ_3 -O(O(5) and O(5')) * atoms linked only to the Ni atoms, four butanol molecules (atoms O(15), O(15'), O(16) and O(16')), two acetone molecules (O(14) and O(14')) and eight water molecules (O_w(1) \cdots O_w(4) and O_w(1') \cdots O_w(4')) take part in coordination with the Ni atoms as terminal ligands. The rest of the solvate molecules (10n-BuOH and 2H₂O) are included in the cavities between Ia molecules, and some atoms of the solvate molecules have high temperature factors (Table 3) which probably indicate their statistical disorder.

Four types of the cyclic fragments can be distinguished in the Ni, Si, O framework of molecule Ia (Fig. 2), viz. relatively rigid four-membered nickel oxide cycles (NiO)₂ (**A**), six-membered nickel oxide cycles (NiO)₃ (**B**), six-membered

* Atoms derived by the inversion centre are primed.

Table 2

Main bond angles (degrees) of the nickel–siloxane framework

O(1)Ni(1)O(2)	179.0(3)	O(1)Ni(3)O(4)	86.8(3)
O(1)Ni(1)O(3)	93.8(3)	O(1)Ni(3)O(6)	85.8(3)
O(1)Ni(1)O(4)	84.5(3)	O(1)Ni(3)O _w (1)	90.1(3)
O(1)Ni(1)O(5)	97.5(3)	O(1)Ni(3)O _w (2)	86.0(3)
O(1)Ni(1)O(5')	83.3(3)	O(1)Ni(3)O _w (3)	176.2(4)
O(2)Ni(1)O(3)	85.2(3)	O(4)Ni(3)O(6)	95.2(4)
O(2)Ni(1)O(4)	95.4(3)	O(4)Ni(3)O _w (1)	174.2(4)
O(2)Ni(1)O(5)	82.8(3)	O(4)Ni(3)O _w (2)	84.3(4)
O(2)Ni(1)O(5')	97.7(3)	O(4)Ni(3)O _w (3)	96.3(4)
O(3)Ni(1)O(4)	90.8(3)	O(6)Ni(3)O _w (1)	89.5(4)
O(3)Ni(1)O(5)	94.8(3)	O(6)Ni(3)O _w (2)	171.8(4)
O(3)Ni(1)O(5')	174.3(3)	O(6)Ni(3)O _w (3)	96.1(4)
O(4)Ni(1)O(5)	174.0(3)	O _w (1)Ni(3)O _w (2)	90.6(4)
O(4)Ni(1)O(5')	93.8(3)	O _w (1)Ni(3)O _w (3)	86.6(4)
O(5)Ni(1)O(5')	80.8(3)	O _w (2)Ni(3)O _w (3)	92.1(4)
O(1)Ni(2)O(2')	96.2(3)	O(2)Ni(4)O(3)	87.5(3)
O(1)Ni(2)O(5')	83.7(3)	O(2)Ni(4)O(7')	82.0(3)
O(1)Ni(2)O(6)	83.3(3)	O(2)Ni(4)O(15)	96.5(4)
O(1)Ni(2)O(7)	177.8(3)	O(2)Ni(4)O(16)	176.1(4)
O(1)Ni(2)O(14)	86.6(3)	O(2)Ni(4)O _w (4)	88.3(3)
O(2)Ni(2)O(5')	84.4(3)	O(3)Ni(4)O(7')	94.6(3)
O(2)Ni(2)O(6)	179.3(3)	O(3)Ni(4)O(15)	173.0(4)
O(2)Ni(2)O(7)	81.6(3)	O(3)Ni(4)O(16)	89.4(4)
O(2)Ni(2)O(14)	95.9(3)	O(3)Ni(4)O _w (4)	86.3(4)
O(5')Ni(2)O(6)	95.2(3)	O(7')Ni(4)O(15)	91.7(4)
O(5')Ni(2)O(7)	96.2(3)	O(7')Ni(4)O(16)	96.0(4)
O(5')Ni(2)O(14)	170.3(4)	O(7')Ni(4)O _w (4)	170.2(4)
O(6)Ni(2)O(7)	99.0(4)	O(15)Ni(4)O(16)	86.8(4)
O(6)Ni(2)O(14)	84.5(3)	O(15)Ni(4)O _w (4)	88.1(4)
O(7)Ni(2)O(14)	93.5(4)	O(16)Ni(4)O _w (4)	93.8(4)
Ni(1)O(1)Ni(2)	93.5(3)	Ni(1)O(4)Si(5)	119.6(5)
Ni(1)O(1)Ni(3)	92.4(3)	Ni(3)O(4)Si(5)	121.1(5)
Ni(1)O(1)Si(1)	117.5(5)	Ni(1)O(5)Ni(1')	99.2(4)
Ni(2)O(1)Ni(3)	92.4(3)	Ni(1)O(5)Ni(2)	98.8(4)
Ni(2)O(1)Si(1)	121.9(5)	Ni(1')O(5)Ni(2)	99.5(4)
Ni(3)O(1)Si(1)	130.2(5)	Ni(2)O(6)Ni(3)	98.5(4)
Ni(1)O(2)Ni(2')	93.9(3)	Ni(2)O(6)Si(6)	120.6(5)
Ni(1)O(2)Ni(4)	91.8(3)	Ni(3)O(6)Si(6)	122.5(5)
Ni(1)O(2)Si(4)	119.2(5)	Ni(2)O(7)Ni(4')	100.9(4)
Ni(2')O(2)Ni(4)	95.4(3)	Ni(2)O(7)Si(3')	122.7(5)
Ni(2')O(2)Si(4)	121.3(5)	Ni(4')O(7)Si(3')	120.6(5)
Ni(4)O(2)Si(4)	127.0(5)	Si(1)O(8)Si(2)	139.2(6)
Ni(1)O(3)Ni(4)	95.5(4)	Si(2)O(9)Si(3)	133.0(6)
Ni(1)O(3)Si(2)	123.0(5)	Si(3)O(10)Si(6')	137.6(7)
Ni(4)O(3)Si(2)	118.9(5)	Si(1')O(11)Si(4)	141.0(6)
Ni(1)O(4)Ni(3)	96.4(4)	Si(4)O(12)Si(5)	140.5(6)
		Si(5)O(13)Si(6)	134.3(7)

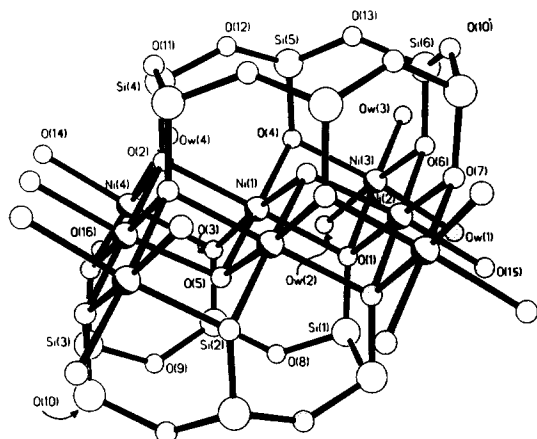
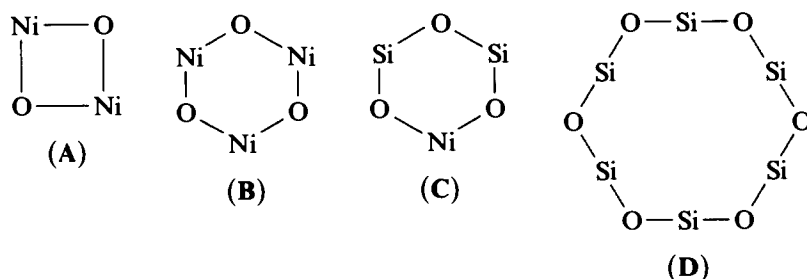
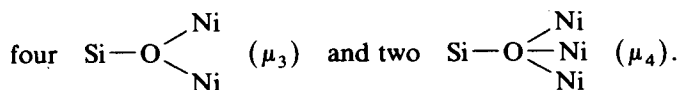


Fig. 2. Ni,Si,O framework of molecule Ia.

nickelasiloxane cycles $\text{NiO}(\text{SiO})_2$ (C) and 12-membered hexasiloxane cycles $(\text{SiO})_6$ (D).



All eight Ni atoms of the nickel oxide layer Ni_8O_8 are approximately coplanar (maximum deviation from the mean-square plane $\Delta_{\text{max}} = 0.05 \text{ \AA}$). The nickel oxide layer is situated between two D siloxane cycles, each linked to the nickel oxide layer by six silanolate bridges, i.e.



The D cycles (whose mean planes are obviously parallel owing to the inversion centre in molecule Ia) are shifted by ca. 1.6 \AA relative to each other parallel to the nickel oxide layer along the vector $\text{Ni}(2) \cdots \text{Ni}(2')$ (Fig. 2 and 3).

The nickel oxide cycles A are planar ($\Delta_{\text{max}} = 0.03 \text{ \AA}$). All six six-membered nickel oxide cycles B have an almost ideal chair conformation (Table 4); conformation assignment was made according to Zefirov and Palyulin [5]. Four of the six symmetrically independent six-membered nickelasiloxane cycles C have a distorted half-boat conformation; the two other have a distorted boat conformation (Table 4). The 12-membered siloxane cycle D has a crown conformation, which is easily seen by the values of the torsion angles SiOSiO (Table 5). However, in structure I the ideal crown symmetry $6m$ is lowered to m (Fig. 3).

Table 3

Atomic coordinates ($\times 10^4$) and isotropic equivalent thermal parameters B_{eq} (\AA^2) in structure I

Atom	x	y	z	B_{eq}	Atom	x	y	z	B_{eq}
Ni(1)	58(1)	4873(1)	4272(1)	1.65(6)	O(9)	-134(5)	6421(3)	3485(4)	2.2(3)
Ni(2)	-1270(1)	4302(1)	4614(1)	1.77(6)	O(10)	516(5)	6937(4)	4727(5)	2.6(4)
Ni(3)	-1107(1)	4027(1)	3221(1)	2.07(6)	O(11)	2174(5)	4513(4)	6087(4)	2.3(3)
Ni(4)	1324(1)	5447(1)	3917(1)	2.06(6)	O(12)	1544(5)	3939(3)	4884(4)	2.2(3)
Si(1)	-1828(2)	5259(2)	3361(2)	2.0(1)	O(13)	358(5)	3274(4)	4580(5)	2.3(3)
Si(2)	-505(2)	5839(2)	3092(2)	2.1(1)	O(14) ^a	2601(5)	5520(4)	4299(5)	3.2(4)
Si(3)	743(2)	6599(2)	4152(2)	2.3(1)	O(15) ^b	-2544(5)	4210(3)	3954(5)	2.8(3)
Si(4)	1971(2)	4519(2)	5228(2)	2.0(1)	O(16) ^b	1210(5)	5892(4)	3037(5)	3.4(4)
Si(5)	751(2)	3698(2)	4215(2)	2.1(1)	O(17) ^b	1529(7)	2844(5)	6657(7)	6.8(6)
Si(6)	-565(2)	3153(2)	4475(2)	2.3(1)	O(18) ^b	1671(7)	1819(5)	6812(6)	8.3(5)
O(1)	-1248(5)	4739(3)	3715(4)	1.7(3)	O(19) ^b	1104(7)	6100(5)	8658(6)	7.4(5)
O(2)	1365(5)	5013(3)	4812(4)	1.7(3)	O(20) ^b	1146(8)	4789(7)	1176(7)	11.3(7)
O(3)	76(5)	5334(3)	3432(4)	2.0(3)	O(21) ^b	31(12)	6076(7)	9146(8)	14(1)
O(4)	126(5)	4166(3)	3752(4)	1.9(3)	O _w (1)	-2407(5)	3961(4)	2616(5)	2.9(4)
O(5)	40(5)	5529(3)	4889(4)	1.9(3)	O _w (2)	-1062(5)	4529(4)	2425(4)	2.8(3)
O(6)	-1168(5)	3642(3)	4052(4)	2.3(3)	O _w (3)	-1038(6)	3331(4)	2667(5)	4.9(5)
O(7)	-1297(5)	3920(3)	5472(4)	1.9(3)	O _w (4)	1389(5)	4715(4)	3446(5)	2.8(4)
O(8)	-1333(5)	5748(3)	3202(4)	2.1(3)	O _w (5)	163(18)	5380(11)	9820(15)	33(2)
C(1) ^c	-2772(8)	5162(5)	2479(7)	2.6(5)	C(19)	2976(8)	4496(5)	5184(7)	2.1(5)
C(2)	-3533(8)	5044(6)	2490(8)	3.5(6)	C(20)	3646(9)	4802(6)	5669(8)	4.0(6)
C(3)	-4250(9)	4998(7)	1832(8)	4.5(6)	C(21)	4404(9)	4766(8)	5642(9)	5.2(7)
C(4)	-4224(10)	5051(6)	1169(8)	4.8(7)	C(22)	4480(9)	4449(7)	5129(10)	5.3(8)
C(5)	-3471(10)	5153(7)	1150(8)	4.6(7)	C(23)	3798(10)	4138(6)	4628(9)	4.5(8)
C(6)	-2739(9)	5220(6)	1804(7)	3.5(6)	C(24)	3041(8)	4177(6)	4659(8)	3.4(6)
C(7)	-841(8)	5937(5)	2090(7)	2.6(5)	C(25)	1121(8)	3289(6)	3662(7)	3.0(6)

C(8)	-1240(8)	6433(6)	1802(7)	3.8(6)	C(26)	925(10)	3423(6)	2942(8)	4.2(7)
C(9)	-1568(11)	6513(8)	1041(10)	6.3(9)	C(27)	1200(11)	3115(9)	2531(9)	6.4(8)
C(10)	-1475(10)	6105(8)	606(9)	5.7(8)	C(28)	1732(12)	2662(7)	2890(11)	6.9(9)
C(11)	-1028(10)	5631(7)	908(8)	4.7(7)	C(29)	1928(11)	2538(8)	3608(10)	6.1(9)
C(12)	-722(9)	5542(6)	1651(7)	3.5(6)	C(30)	1622(9)	2847(6)	3985(9)	4.1(7)
C(13)	1262(8)	7082(6)	3815(7)	2.9(6)	C(31)	-846(7)	2494(6)	3989(7)	2.6(5)
C(14)	1412(12)	7581(8)	2838(10)	6.6(9)	C(32)	-243(10)	2208(7)	3900(10)	5.3(8)
C(15)	2161(11)	7785(7)	3366(10)	5.9(9)	C(33)	-395(11)	1703(7)	3555(10)	6.1(9)
C(16)	960(10)	7219(7)	3073(8)	4.7(7)	C(34)	-1202(11)	1509(7)	3289(9)	5.6(8)
C(17)	2496(11)	7646(7)	4127(10)	6.4(9)	C(35)	-1811(10)	1792(7)	3345(10)	5.4(8)
C(18)	2014(10)	7298(6)	4342(9)	4.8(7)	C(36)	-1629(10)	2288(6)	3705(9)	4.8(7)
C(37) ^d	1207(8)	5666(7)	2429(7)	5.1(6)	C(53)	226(12)	1591(9)	6183(12)	9(1)
C(38)	1146(10)	6157(7)	1909(8)	4.5(7)	C(54)	-440(14)	1384(11)	5458(13)	11(1)
C(39)	1237(7)	5230(4)	2301(6)	1.2(4)	C(55)	-1177(14)	1275(11)	5465(12)	12(1)
C(40) ^e	3018(9)	5951(6)	4133(8)	3.7(6)	C(56)	2059(20)	6298(12)	9276(17)	17(2)
C(41)	3290(9)	5778(6)	3556(8)	3.9(6)	C(57)	2161(18)	5827(11)	9608(15)	14(2)
C(42)	3652(11)	6251(8)	3353(9)	6.5(8)	C(58)	1821(16)	1034(11)	4712(13)	15(1)
C(43)	3861(13)	6099(9)	2724(11)	9(1)	C(59)	1512(15)	638(13)	4307(15)	15(2)
C(44)	-2928(8)	3740(7)	4096(9)	5.5(7)	C(60)	1902(17)	4759(13)	1245(13)	16(2)
C(45)	-3865(10)	3751(9)	3486(12)	9.7(9)	C(61)	2400(14)	4445(12)	1926(16)	17(2)
C(46)	-4305(13)	3280(12)	3640(17)	17(2)	C(62)	1875(20)	9361(15)	2972(18)	21(2)
C(47)	924(17)	2138(13)	8416(18)	19(2)	C(63)	1167(17)	9326(14)	2344(15)	19(2)
C(48)	2028(11)	3137(8)	6365(10)	6.9(9)	C(64)	224(20)	6251(10)	9850(15)	16(2)
C(49)	2722(11)	2790(8)	6463(11)	7.0(9)	C(65)	288(22)	6780(10)	9802(15)	20(2)
C(50)	3264(12)	3124(9)	6243(11)	11(1)	C(66)	149(22)	7121(13)	49(19)	22(2)
C(51)	3986(17)	2933(12)	6459(14)	13(2)	C(67)	557(22)	7677(14)	377(18)	23(2)
C(52)	1001(16)	1622(10)	6141(14)	11(1)					

^a Atom of an acetone molecule. ^b These seven atoms belong to butanol molecules. ^c Atoms C(1)–C(36) belong to Ph-substituents at Si atoms. ^d Atoms C(37)–C(39) belong to an acetone molecule. ^e Atoms C(40)–C(67) belong to butanol molecules.

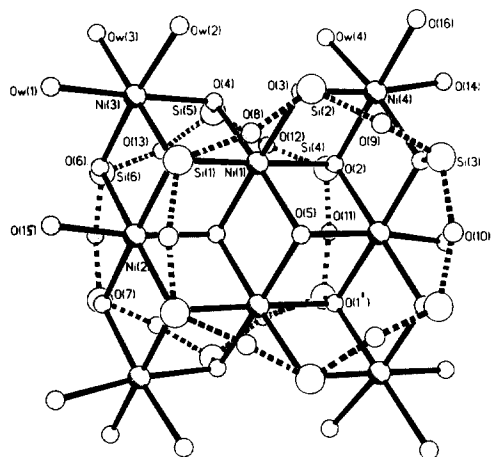


Fig. 3. Projection of the Ni,Si,O framework of molecule Ia onto the mean plane of the nickel oxide layer. Si-O bonds of the siloxane cycles are shown by dashed lines (upper cycle by thick lines, lower cycle by thin lines).

Table 4
Conformations of the B- and C-type cycles

Type	Cycles	Folding parameters [5]			Cycle conformation
		θ (deg.)	ϕ (deg.)	Q (Å)	
B	Ni(1)O(4)Ni(3)O(6)Ni(2)O(5')	179	188	1.62	chair
B	Ni(1)O(5)Ni(2')O(7')Ni(4)O(3)	1	196	1.61	chair
B	Ni(1)O(5)Ni(1')O(2')Ni(2)O(1)	179	333	1.61	chair
B	Ni(1)O(2)Ni(2')O(1')Ni(1')O(5')	1	38	1.62	chair
B	Ni(2)O(5')Ni(1')O(3')Ni(4')O(7)	1	103	1.61	chair
C	Ni(2)O(7)Si(3')O(10')Si(6)O(6)	159	77	0.64	distorted half-boat
C	Ni(3)O(4)Si(5)O(13)Si(6)O(6)	157	78	0.74	distorted half-boat
C	Ni(4')O(7)Si(3')O(9')Si(2')O(3)	146	100	0.75	distorted half-boat
C	Ni(1)O(1)Si(1)O(8)Si(2)O(3)	57	267	0.71	distorted boat
C	Ni(2)O(2')Si(4)O(11')Si(1)O(1)	51	29	1.35	distorted boat
C	Ni(1')O(2')Si(4)O(12')Si(5')O(4')	162	170	1.45	distorted half-boat

Table 5
Torsion angles (deg.) in the D cycle

Si(1)O(8)Si(2)O(9)	-143	Si(6')O(13')Si(5')O(12')	-135
O(8)Si(2)O(9)Si(3)	121	O(13')Si(5')O(12')Si(4')	129
Si(2)O(9)Si(3)O(10)	-128	Si(5')O(12')Si(4')O(11')	-128
O(9)Si(3)O(10)Si(6')	108	O(12')Si(4')O(11')Si(1)	101
Si(3)O(10)Si(6')O(13')	-105	Si(4')O(11')Si(1)O(18)	-99
O(10)Si(6')O(13')Si(5')	138	O(11')Si(1)O(8)Si(2)	141

Coordination of the nickel atoms

All four independent Ni atoms in molecule Ia have octahedral coordination with O atoms of different types. The Ni(1) atom is coordinated by two μ_3 -oxide atoms (O(5) and O(5')) and four silanolate oxygens (μ_3 -O(4), μ_4 -O(2) of one and μ_3 -O(3), μ_4 -O(1) of the other siloxanolate "lid"), the Ni(2) atom by one μ_3 -oxide (O(5')), four silanolate atoms (μ_3 -O(6), μ_3 -O(7) and μ_4 -O(1), μ_4 -O(2) of the "top" and "bottom" lids, respectively) and a butanol O(15) atom, the Ni(3) atom by three silanolate atoms (μ_3 -O(4), μ_3 -O(6) and μ_4 -O(1) of the top and bottom lids, respectively) and three water molecules (O_w(1), O_w(2) and O_w(3)), the Ni(4) atom also by three silanolate atoms (μ_4 -O(2) and μ_3 -O(3), μ_3 -O(6) of the top and bottom lids, respectively), a butanol O(16) atom, an acetone O(14) atom and an H₂O molecule O_w(4).

The Ni–O distances in molecule Ia (Table 1) vary from 2.006 to 2.176(9) Å, being close to the distance 2.097(1) Å in the NiO structure [6] and other nickel compounds with octahedral coordination (e.g. 2.07–2.10(1) Å [7]). The NiO distances can be divided into three groups, viz. the shortest 2.006–2.076(9) Å to μ_3 -O atoms, 2.103–2.176(9) Å to μ_4 -O atoms and 2.088–2.150(10) Å to O atoms of the terminal ligands.

The Ni···Ni distances in the nickel oxide layer (3.073(3)–3.156(2) Å) are close to those in the NiO structure (2.98(1) Å [6]) and known cage-like structures of nickel compounds (e.g. 3.164(1)–3.180(2) Å [7] and 3.087(2)–3.176(2) Å [8]).

The nickel oxide layer Ni₈O₈ in structure I, with its own symmetry 2/m, can be considered as a portion of a "parquet" formed by 6 Ni₃O₄ "cubes" fused through common faces and edges. Each cube is formed by three Ni atoms and four O atoms alternating in the neighbouring vertices, i.e. the cubes are not completed, as one Ni vertex is absent (Fig. 4). The Ni₃O₄ cubes are of two types, viz. two "inner" (including Ni(1) and Ni(1') atoms and oxide atoms O(5) and O(5')) and four "outer" cubes. The inner cubes have a common face, Ni(1)O(5)Ni(1')O(5'), and four common vertices Ni(1), Ni(1'), Ni(2) and Ni(2') with four outer cubes. Each of the four outer cubes has one common face with one of the inner cubes and two

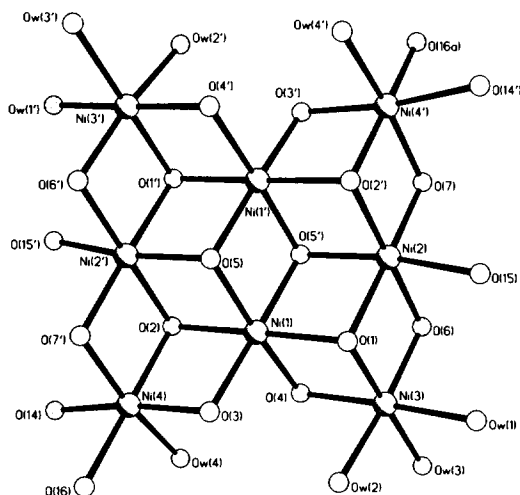


Fig. 4. Projection of the nickel oxide layer onto its mean plane.

common vertices with another outer cube. The bond angles (Table 2) at the vertices of cubes of both types are markedly distorted in comparison with the ideal value of 90° : in the inner cubes the NiONi and ONiO angles are $93.5(3)$ – $99.5(4)^\circ$ and $82.8(3)$ – $97.7(3)^\circ$, respectively; in the outer cubes these angles are $91.8(3)$ – $100.9(4)^\circ$ and $82.0(3)$ – $95.2(3)^\circ$, respectively.

The structure of the inner nickel oxide layer in molecule Ia is identical to a fragment (a portion of the layer one Ni atom thick) of the NiO crystal structure (of the NaCl structural type, space group $Fm\bar{3}m$, $a = 4.1946 \text{ \AA}$ [6]) parallel to the (111) plane, i.e. normal to the 3 axis. A good fulfillment of the symmetry of local 3 axes passing through the Ni atoms normal to the nickel oxide layer of molecule Ia is clear from Fig. 4.

Coordination of Si and O atoms

The Si atoms have a valence configuration close to ideal tetrahedral, with the exception of atoms Si(1) and Si(4). The bond angles at these atoms are significantly distorted: O(1)Si(1)C(1), $117.8(6)^\circ$; O(11)Si(1)C(1), $103.9(6)^\circ$; O(2)Si(4)C(19), $116.8(6)^\circ$; O(12)Si(4)C(9), $103.9(6)^\circ$. This peculiarity of the Si(1) and Si(4) configuration is apparently caused by tetrahedral coordination of the μ_4 -atoms O(1) and O(2) bonded to them (see below). The average Si–O(Si) bond length of $1.637(9) \text{ \AA}$ is larger than that of Si–O(Ni), $1.618(7) \text{ \AA}$. A similar shortening of Si–O(Co) bonds as compared to Si–O(Si) bonds was observed in the cobaltasiloxane II [4].

Oxygen atoms in structure I are characterized by differences in their coordination by Ni atoms, with coordination numbers N_{Ni} from 0 to 3. The endocyclic oxygen atoms of the hexasiloxane cycles and the $O_w(5)$ atom of one H_2O molecule do not coordinate Ni atoms ($N_{\text{Ni}} = 0$). For $O_w(1)$, $O_w(2)$, $O_w(3)$ and $O_w(4)$ of the other H_2O molecules $N_{\text{Ni}} = 1$. The O(15) and O(16) atoms of two butanol molecules have $N_{\text{Ni}} = 1$, whereas the other butanol molecules are characterized by $N_{\text{Ni}} = 0$, while for acetone molecules $N_{\text{Ni}} = 1$. The oxygen atoms of the nickel oxide layer have $N_{\text{Ni}} = 2$ (for 4 silanolate atoms of each hexasiloxanolate cycle) and $N_{\text{Ni}} = 3$ (for 2 silanolate atoms of each such cycle and both oxide oxygen atoms).

It is necessary to consider in more detail the coordination of the O atoms of the nickel oxide layer. Both inner oxide atoms O(5) and O(5') have trigonal pyramidal μ_3 -coordination with respect to Ni (bond angles Ni(1)O(5)Ni(1'), $99.2(4)^\circ$; Ni(1)O(5)Ni(2'), $98.4(4)^\circ$; Ni(1')O(5)Ni(2'), $99.5(4)^\circ$; O(5) atom displacement from the Ni(1)Ni(1')Ni(2') plane $0.99(1) \text{ \AA}$). A similar pyramidal geometry for oxygen atoms is observed, for instance, in the tetranuclear complex $[\text{Ni}(\text{OMe})(2,4,6\text{-Cl}_3\text{C}_6\text{H}_2\text{O})(\text{MeOH})_4]$ [9]. The silanolate atoms O(3), O(4), O(6) and O(7) also have a triple (2Ni + Si)-coordination, but with a more flattened (as compared to O(5)) pyramidal geometry (the maximum O atom displacement from the NiNiSi plane is 0.6 \AA). A fourfold (3Ni + Si)-coordination is typical of the silanolate O(1) and O(2) atoms only. As was mentioned above, such O atoms bonding with three Ni atoms is apparently the reason for the distortion of the tetrahedral configuration of the Si(1) and Si(4) atoms.

Non-coordinating solvate molecules and hydrogen bonds

Two of the five symmetrically independent solvate butanol molecules, not coordinated to Ni atoms, are linked with O_w of the terminal H_2O ligands of molecule Ia by O–H \cdots O hydrogen bonds: $O_w(1) \cdots O(18)_{\text{BuOH}}$ ($1/2 + x$, $1/2 - y$, $1/2 + z$)

2.62(1) Å, O_w(2) ··· O(19)_{BuOH} (-x, 1-y, 1-z) 2.70(1) Å, O_w(3) ··· O(19)_{BuOH} (-x, 1-y, 1-z) 3.02(1) Å. Hydrogen bonds O-H ··· O also join the rest of the solvate butanol molecules (three symmetrically independent ones) and a water molecule (symmetrically independent): O(17)_{BuOH} ··· O(18)_{BuOH} 2.57(1) Å, O(20)_{BuOH} ··· O(21)_{BuOH} (-x, 1-y, 1-z) 2.91(1) Å, O(20)_{BuOH} ··· O_w(5) (x, y, -1+z) 2.95(1) Å.

Thus an extended system of hydrogen bonds is observed in structure I. However, a detailed analysis of the system is impossible, as the hydrogen atoms were not located objectively.

Experimental

Preparation of nickel oxide-siloxanolate complex (I)

Sodium phenylsilanolate (0.1 mol), prepared according to the procedure described in [10], was dissolved in a mixture of butanol (80 ml) and toluene (20 ml). Anhydrous nickel chloride (0.5 mol) was added to the solution obtained. The reaction mixture was heated to boiling and boiled for 2 h. The hot reaction solution was filtered to separate sodium chloride. Light-green crystals were precipitated as the filtrate cooled. They were separated from the mother solution and dried in a vacuum (20 mmHg) at 100°C. 4.4 g (25.4%) of light-green powder was obtained (composition: C 40.12; H 4.50; Si 12.56; Ni 16.98%). The product was recrystallized from aqueous acetone (5% H₂O) and then from butanol. The crystals of I obtained were used for an X-ray structural study. The empirical formula of compound I (according to X-ray crystal study data) was as follows: C₁₃₄H₂₃₂Ni₈O₅₂Si₁₂; calc. (%): C 47.22, H 6.73, Si 9.68, Ni 13.48.

The difference between the calculated composition and that found may be explained by the fact that the analyzed product was dried in a vacuum. Thus it is naturally characterized by a lower content of coordinating solvents.

X-ray crystal structure study

Light-green crystals I are monoclinic, at -120°C: *a* = 18.32(1), *b* = 24.896(15), *c* = 20.55(1) Å; β = 116.30(5)°, *V* = 8403(9) Å³, *d*_{calc} = 1.37 g/cm³, *Z* = 2(C₇₂H₆₀Ni₈Si₁₂O₂₆ · 14C₄H₉OH · 10H₂O · 2(CH₃)₂CO), space group *P*2₁/*n*.

Until cell parameters and intensities of 8441 reflections were measured with a Syntex P2₁ diffractometer at -120°C (λ(Mo-K_α), graphite monochromator, θ/2θ-scan, θ_{max} = 20°). The structure was solved by a direct method and refined by a full-matrix least-squares method. Hydrogen atoms were not located. Final discrepancy factors for 6371 reflections with *I* > 2σ(*I*) are equal to *R* = 0.073 and *R*_w = 0.097. Atomic coordinates are given in Table 3. All calculations were carried out on an Eclipse S/200 computer using the INEXTL programs [11].

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